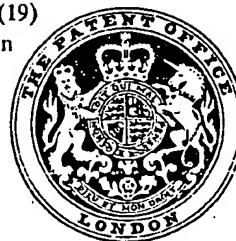


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 (72) Inventors: JACOBUS HENDRIKUS BREUKER  
 HUBERTUS NICOLAAS HERMANUS DE HAAN  
 PIETER BARTELD KWANT  
 ANTON VAN DER WIEL



## (54) PROCESS FOR THE PREPARATION OF LUBRICATING OILS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the preparation of lubricating oils with a viscosity index (VI) lower than 90, namely oils with a low viscosity index (LVI oils, VI < 30) and oils with a medium viscosity index (MVI oils, VI varying between 30 and 90). (The viscosity indices mentioned in this specification relate to values determined by ASTM method D 2270-64). Such oils may be used in all cases in which the VI is not of vital importance, for instance in industry.

For the preparation of HVI oils (high VI, i.e. VI of at least 90) waxy crude oils are used as the feed, since it is possible to prepare from naphthenic crude oils lubricating oils with the desired viscosity index by conventional processes, such as distillation, deasphalting, extraction and dewaxing.

MVI and LVI oils are normally prepared from naphthenic crude mineral oils by application of the following processing stages: distillation, extraction (only for MVI oils) and, if desired, a terminal treatment, for instance an acid or hydrogen treatment.

The term "waxy crude oils" relates to crude mineral oils containing a considerable quantity of paraffins having a melting point above 15°C. Distillate and residual fractions of waxy crude oils containing such paraffins indeed have a relatively high pour point and removal of the paraffins is necessary for the preparation of fuel and lubricating oils that can be used at ambient or at a lower temperature.

The term "naphthenic crude oils" relates to crude mineral oils containing no or hardly any paraffins with a melting point above 15°C. Indeed, fuel oils and lubricating oils prepared from naphthenic crude oils need not be dewaxed.

MVI and LVI oils are generally prepared by blending vacuum distillate fractions prepared from a naphthenic crude oil; these fractions are denoted by a number that is equal to their viscosity in seconds Redwood at 140°F. Examples of fractions are LVI 50, LVI 140, LVI 450, LVI 700 and LVI 1100. If an MVI oil has to be prepared from one or more of these fractions, the VI should be increased somewhat. This can be achieved by partly removing by extraction the aromatic compounds of one or more of the fractions to be included in the MVI oil.

Since the availability of naphthenic crude oils may become a problem, it would be attractive if the distillate fractions for the preparation of LVI and MVI lubricating oils obtained from naphthenic crude oils could be replaced by other components. Naturally, such a replacement should not unduly affect the properties of the lubricating oil, such as colour and colour stability.

In areas only having facilities for HVI lubricating oil manufacture, it would be particularly advantageous if MVI and/or LVI lubricating oils could be prepared from the HVI feed, since the transport of fractions from a naphthenic crude oil from the place of production to the area concerned may be a difficult and costly affair. It would be especially advantageous if MVI and LVI lubricating oils could be prepared from a waxy crude oil without an appreciable drop in the yield of HVI lubricating oil prepared from this feed.

The criterion to be met by such an MVI and/or LVI lubricating oil to be prepared from an

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HVI lubricating oil feed is that the viscometric and colour properties should be comparable with those of MVI and/or LVI lubricating oils prepared entirely from a naphthenic crude mineral oil as the feed.

Normally, the preparation of HVI lubricating base oils is carried out as follows. A waxy crude mineral oil is separated by distillation at atmospheric pressure into a number of distillate fractions (viz. in succession, one or more gasoline, kerosine and light gas oil fractions) and a residuc (called the long residuc). By distillation at reduced pressure this long residuc is subsequently separated into a number of distillate fractions (viz. in succession, one or may heavy gas oil, spindle oil, light machine oil and medium machine oil fractions) and a residuc (called the short residuc). From the lubricating oil fractions obtained in the distillation at reduced pressure the corresponding lubricating oils are prepared by refining. Refining of the spindle oil, light machine oil and medium machine oil fractions takes place by removal of at least part of the aromatics and paraffins from these fractions. In the refining of the short residuc first of all asphalt is removed from the residuc.

From the deasphalted oil thus obtained at least part of the aromatics and paraffins is subsequently removed. The residual lubricating oil thus prepared is referred to as bright stock. The processes for the removal of asphalt, aromatics and paraffins are called hereinafter: deasphalting, aromatics extraction and dewaxing.

In the preparation of a lubricating base oil from a residual lubricating oil fraction deasphalting is carried out because the presence of asphalt in lubricating oils is undesirable and because it also interferes with subsequent refining treatments.

The aim of the aromatics extraction is to increase the viscosity index and to improve the colour as well as the oxidation and colour stability of the fractions. The aromatic extracts are by-products of the HVI lubricating oil preparation and they have little value. They are generally used as fuel components.

Dewaxing reduces the pour point of the lubricating oil fractions, thus making them suitable for use at temperatures lower than ambient temperature.

The aromatic extracts described hereinbefore, which generally have a relatively low VI, are, as far as their viscosity properties are concerned, suitable for use as components for MVI and LVI oils. However, the aromatic extracts generally have an unattractive colour as well as a poor colour stability. Consequently, they are not used as lubricating oil components in cases where a light colour and/or a good colour stability are desirable.

It is known from Specification 1.390.953 that the colour as well as the colour stability of aromatic extracts from both distillate and deasphalted residual lubricating oil fractions derived from crude mineral oils can be considerably improved by subjecting these extracts to a catalytic hydrogen treatment. It is furthermore known that after this catalytic hydrogen treatment the aromatic extracts are eminently suitable for use as blending components for the preparation of LVI and MVI oils based completely on waxy starting materials. It has been found, that apart from the above-mentioned hydrogen-treated aromatic extracts dewaxed gas oils can also be included in the blends, provided that these gas oils have a 5% boiling point of at least 275°C and have been obtained in the distillation of waxy crude mineral oils. If the preparation of the LVI and MVI oils use is made of one or more dewaxed gas oils, these gas oils may be blended with either one or more hydrogen-treated aromatic extracts of distillate lubricating oil fractions, or with one or more hydrogen-treated aromatic extracts of residual lubricating oil fractions, or with a blend of one or more hydrogen-treated aromatic extracts from each of the aforementioned categories.

The present patent application therefore relates to a process for the preparation of lubricating oils with a viscosity index lower than 90 by blending two or more components prepared from crude mineral oils, which components have been selected from the following three groups:

- A. aromatic extracts from deasphalted residual lubricating oil fractions, which extracts have been subjected to a catalytic hydrogen treatment.
- B. aromatic extracts from distillate lubricating oil fractions, which extracts have been subjected to a catalytic hydrogen treatment, and
- C. dewaxed gas oil having a 5% boiling point of these fractions are prepared from waxy crude mineral oils, at least 275°C, and characterized in that the lubricating oils are prepared by blending one or more components selected from group C with one or more components selected from group A and/or with one or more components selected from group B.

In the process according to the invention at least one of the blending components must be prepared from an aromatic extract from distillate lubricating oil fraction or from a deasphalted residual lubricating oil fraction. Suitable extractants include furfural, phenol and sulphur dioxide. It is preferred to use furfural for this purpose. Extraction, when applied to a residual lubricating oil fraction, should be preceded by asphalt removal. Deasphalting can very suitably be carried out by contacting the residual lubricating oil

fraction at elevated temperature and pressure with an excess of a lower hydrocarbon such as propane, butane, pentane or a mixture thereof. It is preferred to use propane for this purpose.

In the preparation of lubricating oils according to the invention at least one of the blending components must be an aromatic extract, which extract has been subjected to a catalytic hydrogen treatment. In this specification "a catalytic hydrogen treatment" should be taken to mean a treatment in which the oil concerned is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity. Preference is given to catalysts comprising nickel and/or cobalt and, in addition, molybdenum and/or tungsten on a carrier. Very suitable metal combinations are nickel-molybdenum, cobalt-molybdenum and nickel-tungsten. Preferably, alumina is used as the carrier. The metals may be present in the catalysts in the metallic form or in the form of their oxides or sulphides. Preference is given to the use of catalysts in the sulphidic form. In addition to one or more metals having hydrogenation activity, the catalysts may contain promoters such as fluorine, boron and/or phosphorus. The conditions under which the catalytic hydrogen treatment of the aromatic extracts can be carried out may vary widely. The catalytic hydrogen treatment is preferably carried out at a temperature of 250-425°C and in particular of 300-400°C, a hydrogen partial pressure of 50-200 bar and in particular of 75-175 bar, a space velocity of 0.5-5 kg.l<sup>-1</sup>.h<sup>-1</sup> and in particular of 0.5-2.5 kg.l<sup>-1</sup> and a hydrogen/oil ratio of 250-2500 Nl.kg<sup>-1</sup> and in particular of 500-2000 Nl.kg<sup>-1</sup> (N = normal temperature and pressure). Further, it is preferred for the catalytic hydrogen treatment of the aromatic extracts to be carried out so that after removal of volatile components from the hydrogen-treated product an oil is obtained with a colour according to ASTM-D 1500 of 5 or lighter and in particular of 3.5 or lighter, whose colour rating after 24 hours at 100°C has increased by not more than 3 units and in particular by not more than 1.5 units.

If it is intended in the process according to the invention to use two or more aromatic extracts, these aromatic extracts can be subjected to a catalytic hydrogen treatment before or after mixing.

Suitable gas oils can be obtained in the distillation of waxy crude oil under atmospheric pressure as well as gas oils obtained in the vacuum distillation of waxy crude oils. Preference is given to gas oils whose pour point has been reduced by dewaxing to -10°C or lower and in particular to -15°C or lower. For dewaxing of the gas oils all the methods known in the art are in principle suitable, for instance cooling in the presence of a mixture of methyl ethyl ketone and toluene. As gas oils are obtained on a large scale as by-products in the preparation of wax by dewaxing of gas oils with the aid of urea, preference is given to gas oils dewaxed in this way as blending components for the present lubricating oils. If desired, the gas oils, before being used as blending components, may be subjected to a catalytic hydrogen treatment to improve their colour and colour stability. This catalytic hydrogen treatment may be carried out either before or after dewaxing. Since the gas oils will often originate from a process for the preparation of wax, the catalytic hydrogen treatment will preferably be carried out after dewaxing. The catalysts and conditions that are preferably used in the catalytic hydrogen treatment of gas oils are the same as those mentioned hereinbefore for the aromatic extracts. It may be observed that in the catalytic hydrogen treatment of gas oils special preference is given to temperatures between 300 and 350°C, whereas in the catalytic hydrogen treatment of aromatic extracts of distillate lubricating oil fractions and aromatic extracts from deasphalted residual lubricating oil fractions special preference is given to temperatures between 350 and 375°C and between 375 and 400°C, respectively.

If it is intended to use a gas oil that has been subjected to a catalytic hydrogen treatment, it may be preferable first to blend it with the aromatic extracts to be incorporated in the lubricating oil and to subject the blend to a catalytic hydrogen treatment.

The gas oil will generally have been dewaxed before it is blended with the other components. If desired, dewaxing of the gas oil may be carried out after it has been blended with the other components. This embodiment may be preferred, for instance, when in the preparation of lubricating oil use is made of aromatic extracts having such a high pour point that they must be dewaxed in view of the pour point required for the lubricating oil to be prepared.

As explained hereinbefore the pour point of the lubricating oils prepared according to the invention may be reduced by dewaxing the blending components used and/or dewaxing the blend. A reduction of the pour point of the lubricating oils may also be effected by addition of a pour point reducer. Examples of suitable pour point reducers are condensation products of chlorinated paraffins which chlorinated naphthalene or with phenol and copolymers of ethene and vinyl acetate. Preference is given to polymers with unbranched aliphatic hydrocarbon side chains with at least 16 carbon atoms, such as polymers of alkyl

esters of unsaturated monocarboxylic acids, in particular of acrylic acid and methacrylic acid, in which the alkyl chains are unbranched and contain 16-22 carbon atoms and copolymers of these alkyl esters with other monomers such as vinylpyridines. The amount of pour point reducer that may be added to the LVI and MVI lubricating oils prepared according to the invention may vary within wide limits dependent on the pour-point-reducing effect of the additive concerned and the pour point reduction that is aimed at. In general the amount of pour point reducer applied is 0.01 to 1 %w.

The amounts of the different blending components that can be used in the process according to the invention, may vary within wide limits dependent on the desired viscosity of the lubricating oil to be prepared. For the preparation of lubricating oils with a viscosity Redwood I at 140°F below 200 s, it is preferred to blend 50-98 parts by weight of one or more components selected from group B with 2-50 parts by weight of one or more components selected from group C.

In addition to the pour point reducers mentioned hereinbefore, also other quality-improving additives may be incorporated in the lubricating oils prepared according to the invention. Examples of such additives are antioxidants (e.g. alkylphenols), detergent additives (e.g. calcium petroleum sulphonates, calcium alkylsalicylates and polyamines containing a hydrocarbon chain of at least 50 carbon atoms such as polyisobutenyltetraethylenepentamine) and extreme pressure additives such as zinc dialkyldithiophosphates. Lubricating oils prepared according to the invention have a good colour and colour stability. These properties can be further improved by subjecting the lubricating oils to an activated earth treatment.

The lubricating oils prepared according to the invention may be used for various applications, for instance for automotive engines, gear oils, axle oils, mould oils in concrete and foundry technology, in lubricating greases and printing inks and in the processing of rubbers and fibres.

The invention will now be illustrated with the aid of the following example.

#### Example

From each of two waxy crude oils from the Middle East (Crude oils 1 and 2) a heavy gas oil fraction, three distillate lubricating oil fractions (a spindle oil, a light machine oil and a medium machine oil fraction, respectively) and a residual lubricating oil fraction were isolated by atmospheric distillation followed by vacuum distillation. The heavy gas oil fractions were dewaxed with urea, the distillate lubricating oil fractions were extracted with furfural and the residual lubricating oil fractions were deasphalted with propane and subsequently extracted with furfural. Thus, from each of the crude oils the following oils were prepared: a dewaxed gas oil (DGO), an aromatic extract of a spindle oil (ESO), an aromatic extract of a light machine oil (ELMO), an aromatic extract of a medium oil (EMMO) and an aromatic extract of a residual lubricating oil (ERO). With the exception of the aromatic extract of the residual lubricating oil prepared from crude oil 1, each of the above-mentioned oils (Oils 3-11) was used in the preparation of lubricating oils according to the invention. Some properties of oils 3-11 are collected in Table A.

TABLE A

Oil No.	3	4	5	6	7	8	9	10	11
Type	DGO	ESO	ELMO	EMMODGO	ESO	ELMQ	EMMO	ERO	
Prepared from crude oil No.	1	- 1	1	1	2	2	2	2	2
Colour (ASTM-D 1500)	L 3.0	D 8.0	D 8.0	D 8.0	L 3.0	D 8.0	D 8.0	D 8.0	D 8.0
Colour after 24 h at 100°C	4.5				L 8.0				
Pour point (ASTM-D 97), °C	-30	+9	+18	+27	-24	+12	+18	+30	
Viscosity Redwood I at 140°F, s	40	145	533	902	52	125	410	984	3200
5% Boiling point, °C	290				334				

With the exception of oil 3, all the other oils mentioned in Table A were subjected to a catalytic hydrogen treatment using two catalysts (Catalysts 1 and 2) with the following composition:

- 5      Cat. 1 = Ni/Mo/P/Al<sub>2</sub>O<sub>3</sub> catalyst containing 3.8 pbw nickel, 16.0 pbw molybdenum and 4.0 pbw phosphorus per 100 pbw alumina carrier.      5  
10      Cat. 2 = Ni/W/F/Al<sub>2</sub>O<sub>3</sub> catalyst containing 30.6 pbw nickel, 59.2 pbw tungsten and 10.1 pbw fluorine per 100 pbw alumina carrier.

10      The products obtained in the catalytic hydrogen treatment were topped to remove the lower boiling constituents. In this process topping temperatures were applied varying between 270 and 330°C. The conditions that were applied in the catalytic hydrogen treatment as well as some properties of the oils obtained after hydrogen treatment and topping (Oils 12-24) are collected in Table B.      10

TABLE B •

Oil No.	12	13	14	15	16	17	18	19	20	21	22	23	24
Prepared by H <sub>2</sub> treatment													
of oil No.	4	5	6	7	7	7	8	8	9	10	10	11	11
Conditions at the H <sub>2</sub> treatment													
Cat No.	1	1	1	1	2	2	2	2	2	2	2	2	2
Temper- ature, °C	350	350	350	350	350	350	350	350	350	350	375	350	375
Hydrogen partial pressure, bar	100	100	100	100	100	150	100	150	100	100	150	100	150
Space ve- locity, kg.l <sup>-1</sup> .h <sup>-1</sup>	0.7	0.7	0.7	1.0	0.7	1.0	0.7	0.7	1.0	0.7	0.7	1.0	1.0

TABLE B (cont'd)

Oil No.	12	13	14	15	16	17	18	19	20	21	22	23	24
H <sub>2</sub> oil ratio,													
Nl.kg <sup>-1</sup>	600	600	600	600	600	600	600	600	600	680	665	600	600
H <sub>2</sub> treated product													
topped													
at, °C	270	300	300	270	270	270	270	270	300	300	300	330	330
Colour	2.0	L 3.5	L 3.5	L 0.5	L 0.5	L 0.5	L 2.0	L 1.5	2.5	L 3.0	2.0	L 5.5	L 3.5
Colour after 24 h at 100°C	2.5	4.5	L 0.5	L 0.5	L 0.5	L 0.5	L 3.0	L 2.5	L 4.5	L 5.0	L 5.0	L 6.5	L 7.5
Pour point, °C	-15	+3	+21	-27	-21	-21	+6	+3	+18	+27	+27	+36	+39

Finally, 13 lubricating oils according to the invention (Lubricating oils I-XIII) were prepared by blending two or three oils selected from oils 3, 7, 12-19 and 21-24. In addition, a lubricating oil according to the invention (Lubricating oil XIV) was prepared by blending oils 7 and 8 followed by a catalytic hydrogen treatment of the blend and topping of the hydrogen-treated product at 270°C. The hydrogen treatment of the blend was carried out using cat. 2 at a temperature of 325°C, a hydrogen partial pressure of 150 bar, a space velocity of 0.7 kg.l<sup>-1</sup>.h<sup>-1</sup> and a H<sub>2</sub>/oil ratio of 600 Nl.kg<sup>-1</sup>. By a treatment of lubricating oil XIV with 3%w of activated earth an improvement was effected in the colour and in the colour after 24 h at 100°C, from L 3.0 to L 2.5 and from L 6.0 to L 3.5, respectively.

The compositions of lubricating oils I-XIV as well as some properties of these lubricating oils are collected in Table C. The type of blend of the lubricating oils concerned is also indicated in the table on the basis of the blending components used in the preparation and selected from groups A, B and C, viz.

1. One or more components selected from group C with one or more components selected from group A (type CA),
  2. One or more components selected from group C with one or more components from group B (type CB), and
  3. one or more components selected from group C with one or more components selected from group A and with one or more components selected from group A and with one or more components selected from group B (type CAB).
- All the lubricating oils prepared according to the invention had a VI lower than 90.



TABLE C (cont'd)

Lub. oil No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Type of blend	CA	CA	CB	CB	CB	CB	CB	CB	CB	CB	CB	CAB	CAB	CB
Colour	L 4.5	L 2.0	L 3.0	L 3.5	3.5	L 1.5	2.0	1.5	L 1.5	L 2.0	L 2.0	L 4.5	2.0	L 1.5
Colour after 24 h at 100°C	L 6.0	L 4.0	L 5.0	L 6.5	7.0	2.0	2.5	L 3.0	2.5	L 3.0	L 4.0	L 5.5	3.0	L 2.5
Pour point, °C	-3*	-12*	-27	-15	-15	-24	-15	-21	-18	-9*	-9*	-3*	-15*	-15
Viscosity														
Redwood I at 140°F, s	450	110	51	51	51	51	51	50	50	101	190	650	101	50

\* Pour pint after addition of 0.1 %w of a homopolymer of C<sub>18</sub> alkylacrylate with an average molecular weight of 25,000 as pour point reducer

## WHAT WE CLAIM IS:

1. A process for the preparation of lubricating oils with a viscosity index lower than 90 by blending two or more components prepared from crude mineral oils, which components have been selected from the following three groups:
- 5 A. aromatic extracts from deasphalted residual lubricating oil fractions, which extracts have been subjected to a catalytic hydrogen treatment.
- B. aromatic extracts from distillate lubricating oil fractions, which extracts have been subjected to a catalytic hydrogen treatment.
- 10 C. these fractions are prepared dewaxed gas oil having a 5% boiling point of at least 275°C, characterised in that from waxy crude mineral oils, and that the lubricating oils are prepared by blending one or more components selected from group C with one or more components selected from group A and/or with one or more components selected from group B.
- 15 2. A process according to claim 1, characterized in that the pour point of the gas oil has been reduced by dewaxing to  $-10^{\circ}\text{C}$  or lower.
3. A process according to claim 1 or 2, characterized in that the gas oil has been subjected to a catalytic hydrogen treatment.
- 20 4. A process according to any one of claims 1-3, characterized in that for the preparation of lubricating oils with viscosity Redwood I at  $140^{\circ}\text{F}$  below 200 s. 50-98 pbw of one or more components selected from group B are blended with 2-50 pbw of one or more components selected from group C.
5. A process according to any one of claims 1-4, characterized in that the lubricating oil obtained is subjected to a treatment with activated earth.
- 25 6. A process for the preparation of lubricating oils with a viscosity index lower than 90, substantially as described hereinbefore with particular reference to the example.
7. Lubricating oils with a viscosity index lower than 90 and prepared according to a process as described in any one of claims 1-6.

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R.C. ROGERS.  
Chartered Patent Agent,  
Shell Centre,  
London SE1 7NA.  
Agent for the Applicants.

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